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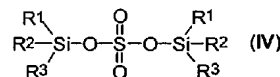
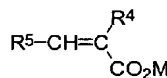
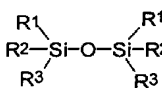
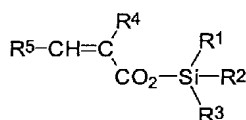
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(54) Title: PROCESS FOR THE PREPARATION OF TRIALKYLSILYLATED CARBOXYLATE MONOMERS, THE OBTAINED TRIALKYLSILYLATED CARBOXYLATE MONOMERS AND THEIR USE IN ANTI-FOULING COATINGS



(57) Abstract: The invention relates to a process for the preparation of trialkylsilylated carboxylate monomers of general formula (I), which process comprises the step of reacting a hexaalkyldisilylsulfate of the formula (IV), with an unsaturated carboxylic compound of formula (III), and the obtained compounds. The invention further relates to a process for the preparation of a hexaalkyldisilylsulfate of the formula (IV) by treating a hexaalkyldisiloxane of formula (II), with fuming sulfuric acid, and the obtained compounds. The invention further relates to the use of said compound (I) in the preparation of a hydrolysable polymer.



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PROCESS FOR THE PREPARATION OF TRIALKYLSILYLATED CARBOXYLATE MONOMERS, THE  
OBTAINED TRIALKYLSILYLATED CARBOXYLATE MONOMERS AND THEIR USE ANTI-FOULING  
COATINGS

Field of the invention

- 5 The invention relates to a new method for the chemical preparation of trialkylsilylated carboxylate monomers. The invention also relates to a process for the preparation of a hexaalkyldisilylsulfate suitable in the process for the preparation of said monomers. The invention further relates to said obtained trialkylsilylated carboxylate monomers and in another aspect, the invention further relates to their use for the synthesis of hydrolysable  
10 polymers, such as binders for modern antifouling coatings.

Background

- Antifouling paints are used to prevent and delay the fouling of underwater structures (e.g. ships' bottom, docks, fishnets, and buoys) by various marine organisms such as shells,  
15 seaweed, and aquatic bacteria. When such marine organisms adhere and propagate on an underwater structure like the bottom of a ship, the surface roughness of the whole ship may be increased to induce decrease of velocity of the ship or increase of fuel consumption. Further, removal of such aquatic organisms from the ship's bottom needs much labour and a long period of working time. In addition, if these organisms adhere and  
20 propagate on an underwater structure such as a steel structure and deteriorates their anticorrosive coating films, the strength or the function of the underwater structure may be lowered and thereby extremely reduce the lifetime of the underwater structure.

- Underwater structures are therefore coated with antifouling paint with excellent antifouling  
25 properties. Recent anti-fouling paints employ polymers containing various hydrolysable groups and more specifically organosilyl groups. Amongst those antifouling paints is for example, an antifouling paint of the hydrolysable self-polishing type proposed in WO 8402915 and JP 63215780 which employs a methacrylic ester polymer having triorganosilyl group in side chains or a similar polymer. Other examples of patents and  
30 patent applications related to the use of organosilyl acrylate polymers in antifouling compositions are EP 131626, US 4593055, US 4594 365, JP 63118381, EP 0775733, WO 9638508, JP 11116257, EP 802243, EP 0714957, JP 07018216, JP 01132668, JP 05077712, JP 01146969 and US 4957989 and hereby incorporated by reference.

Some of the polymers used in the above-described antifouling paints are based on silylated carboxylate monomers.

Several processes are known as conventional techniques for the synthesis of said silylated  
5 carboxylate monomers.

JP 5306290 describes a process to obtain a methacrylic functional group-containing organosilicon compound. The process comprises reacting methacrylic acid with a  
10 halogenoalkylsilane (e.g. trialkylsilylchloride) in the presence of a tertiary amine compound having a cyclic structure. This process may have disadvantages such as the reduced availability and storage stability of the silyl chloride. Moreover, the reaction yields a hydrogen halide or a halide salt as a by-product, which provokes the corrosion of the production equipment.

15 The synthesis of trimethylsilyl methacrylate from methacrylic acid and hexamethyldisilazane is described in footnote 9 of S.Murata and R.Noyori, Tetrahedron Letters, vol.22, n°22, p 2107 (1981).

The Chemical abstract of JP-A-57040493 describes the synthesis of trimethylsilyl  
20 carboxylate, triethylsilyl carboxylate and phenyldimethylsilyl carboxylate from carboxylic acid and hexaorganodisiloxane in the presence of sulfuric or phosphoric acids.

JP 10195084 discloses the reaction of unsaturated carboxylic acid such as acrylic acid or methacrylic acid with a trialkylsilylhydride compound in the presence of a copper catalyst.  
25 One of the disadvantages of this method is the risk of hydrogenation of the unsaturated carboxylic acid due to a side reaction of the produced H<sub>2</sub> on the carbon-carbon double bond.

A first object of the present invention is to provide a novel process capable of readily  
30 preparing trialkylsilylated carboxylate compounds in a high yield from starting materials that are inexpensive and easily available. A second object of the present invention is to provide a novel process offering an improvement vis-à-vis of the disadvantages disclosed above.

Another object of the present invention is to provide for a more direct method for the synthesis of such trialkylsilylated carboxylate compounds, with a more suitable reaction.

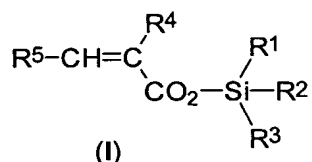
Yet another object of the invention is a process providing for easy work-up procedures.

5 A further object of the invention is a process providing a straightforward purification.

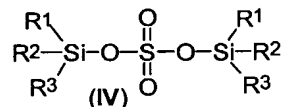
Yet a further object of the invention is a process adaptable for the synthesis of unsaturated, thus being polymerisable, silyl esters involving one or more steps carried out at room temperature. Still a further object is a process avoiding the need to use an inhibitor  
 10 during the monomer synthesis. Still another object is a process avoiding a further purification step.

#### Summary of the invention

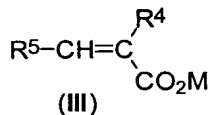
The present invention relates to a new process for the preparation of trialkylsilylated  
 15 carboxylate monomers of general formula (I)



wherein R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> represents each independently an alkyl or an aryl group, R<sup>4</sup> represents a hydrogen atom or a methyl group and R<sup>5</sup> represents a hydrogen, alkyl, -COR<sup>6</sup> or -COOR<sup>6</sup>; wherein R<sup>6</sup> represents an alkyl group, which process comprises the step of  
 20 reacting a hexaalkyldisilylsulfate of the formula (IV)

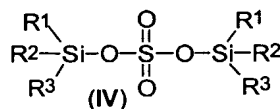


with an unsaturated carboxylic compound of formula (III)

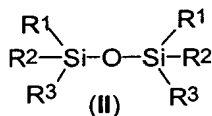


wherein M is a metallic cation and R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> have the same meaning as that  
 25 defined above respectively.

The present invention further relates to a process for the preparation of a hexaalkyldisilylsulfate of the formula (IV)



by treating a hexaalkyldisiloxane of formula (II)



5

with fuming sulfuric acid, wherein  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$  represents each independently an alkyl or an aryl group.

In a preferred embodiment said latter process can precede the first process.

10

In a preferred embodiment  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$  and  $\text{R}^6$  each independently represents a linear, branched or cyclic alkyl group, saturated or unsaturated, containing from 1 to 12 carbon atoms, preferably from 1 to 6 carbon atoms, more preferably from 1 to 4 carbon atoms, yet more preferably 4 carbon atoms.

15

M is preferably chosen from the group comprising  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ba}^{++}$ ,  $\text{Ca}^{++}$  and more preferably  $\text{Na}^+$  and  $\text{K}^+$ .

20

More suitably,  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$  each independently are chosen from the group comprising of methyl, ethyl, propyl, isopropyl, butyl, t-butyl, phenyl or substituted phenyl. Yet in a more preferred embodiment  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$  are butyl or isopropyl.

25

In another embodiment the trialkylsilylated carboxylates of general formula (I) and the unsaturated carboxylic compound (III) can be either of cis (maleic) or trans (fumaric) configuration.

In a more preferred embodiment the trialkylsilylated carboxylates obtained by the process of the invention are preferably trialkylsilyl methacrylates.

The present invention will be further disclosed in detail hereunder. Four examples and figure 1, which is a graph showing the yield versus the weight of 20% fuming sulphuric acid, will elucidate the present invention further in a non-limiting way.

5 Detailed description of the invention

The present invention relates to a new process for the synthesis of trialkylsilylated carboxylates represented by the above-described formula (I).

10 Although the invention will be explained using a two-step reaction, it is clear from the previous description that the invention also relates to each step separately.

In general, the process comprises two steps. These steps can be performed in a one-pot reaction or separate.

15 A preferred embodiment of this method will be elucidated in detail.

In a first step, a hexaalkyldisiloxane represented by the above-described formula (II) is treated with fuming sulfuric acid. Fuming sulfuric acid is a solution of sulfur trioxide in sulfuric acid; in a preferred embodiment, there is used a solution containing 10 to 70 wt% free sulfur trioxide, and in the most preferred embodiment, fuming sulfuric acid  $\text{H}_2\text{SO}_4$  containing about 20% free  $\text{SO}_3$ . At the end of this reaction two layers may be obtained, an upper and a bottom layer. After isolation for example via decantation, the upper layer furnishes the hexaalkyldisilylsulfate formed during the reaction. An alternative process e.g. when there is insufficient phase separation could be treating with a drying agent such as ammonium sulfate.

Hexaalkyldisilylsulfates can also be obtained from the reaction of trialkylsilanes with  $\text{SO}_3$ , as described in M.Weidenbruch et al. (J.Organometallic Chemistry 141 (1977) 9-21).

30 In a second step, the hexaalkyldisilylsulfate obtained in step one is reacted with an unsaturated carboxylic compound represented by the above-described formula (III). The reaction is preferably set up such as each one mole of hexaalkyldisilylsulfate is treated with at least two moles of unsaturated carboxylic compound.

Examples of unsaturated carboxylic compounds which can be used in the process according to the invention include derivatives of acrylic acid, methacrylic acid, maleic acid, fumaric acid and more particularly, acrylic acid, methacrylic acid, maleic acid, fumaric acid, methyl maleic acid, amyl maleic acid, n-butyl maleic acid, methyl fumaric acid, amyl fumaric acid, n-butyl fumaric acid. In a more preferred embodiment said unsaturated carboxylic compound is a methacrylic compound.

- Said unsaturated carboxylic compounds are preferably chosen amongst metal salts. In a more preferred embodiment sodium or potassium salts of said compounds are used.
- At the end of the reaction, the reaction mix is optionally treated with an organic solvent and the precipitate formed is filtered out. The organic solvent is then easily evaporated under reduced pressure and the unsaturated trialkylsilyl carboxylate is isolated, eventually distilled under reduced pressure.
- In another embodiment the two steps of the process are performed under inert atmosphere and more preferably under nitrogen atmosphere.

Examples of the trialkylsilylated carboxylate monomers prepared by the process of the invention using methacrylic acid in step two, include trimethylsilyl methacrylate, triethylsilyl methacrylate, tri-n-propylsilylmethacrylate, triisopropylsilyl methacrylate, tri-n-butylsilyl methacrylate, triisobutylsilyl methacrylate, tri-s-butylsilyl methacrylate, tri-n-amylsilyl methacrylate, tri-n-hexylsilyl methacrylate, tri-n-octylsilyl methacrylate, tri-n-dodecylsilyl methacrylate, triphenylsilyl methacrylate, tri-p-methylphenylsilyl methacrylate, tribenzylsilyl methacrylate and tri t-butylsilyl methacrylate.

Other examples include ethyldimethylsilyl methacrylate, n-butyldimethylsilyl methacrylate, t-butyl dimethylsilyl methacrylate diisopropyl-n-butylsilyl methacrylate, n-octyldi-n-butylsilyl methacrylate, diisopropylstearylsilyl methacrylate, dicyclohexylphenylsilyl methacrylate, t-butyl diphenylsilyl methacrylate, phenyldimethylsilyl methacrylate and lauryldiphenylsilyl methacrylate.

Examples of trialkylsilylated carboxylate monomers of general formula (I) wherein R<sup>5</sup> is the ester of the above-described formula (II) include triisopropylsilyl methyl maleate, triisopropylsilyl amyl maleate, tri-n-butylsilyl n-butyl maleate, t-butyldiphenylsilyl methyl

maleate, t-butyldiphenylsilyl n-butyl maleate, triisopropylsilyl methyl fumarate, triisopropylsilyl amyl fumarate, tri-n-butylsilyl n-butyl fumarate, t-butyldiphenylsilyl methyl fumarate, and t-butyldiphenylsilyl n-butyl fumarate.

- 5 In the existing methods for the preparation of carboxylic acid silyl esters by acid catalysed silylation, continuous removal of water is necessary for shifting the equilibrium towards the product. Furthermore, bulkier silyl groups fail to react in such conditions (see Examples 1 and 2), this probably due to enhanced steric strain associated with low reactivity of some unsaturated carboxylic acid derivatives.

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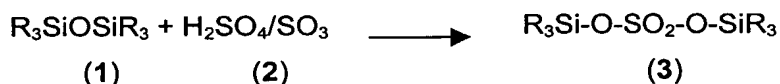
In the process of the present invention fuming sulfuric acid is used in step one. This particular feature provides with the advantages that there is no need to set up a system for continuous removal of water. The yield is increased and the product purification is simplified. Furthermore, another advantage is that reactions may be performed at room  
15 temperature. Due to these mild conditions there is no need to use polymerisation inhibitors and no degradation of the material occurs.

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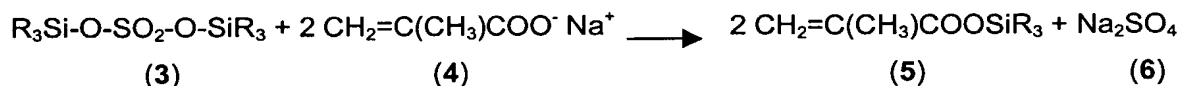
Due to its shortness, its easy work-up procedure and its high yield the process of the present invention can be considered as a substantial improvement over the existing methods described above.

The feasibility of the process of the invention has been proven with the synthesis of tributylsilyl methacrylate (5) (Scheme) in two reaction steps in a very good yield of 73.3%.

25 General scheme:



30



In a first step hexabutylidisiloxane (1) is treated with fuming sulfuric acid (2) under a nitrogen atmosphere to give hexabutylidisilylsulfate (3). In a second step (3) is reacted with at least two equivalent of sodium methacrylate (4) to give tributylsilylmethacrylate (5).



Figure 1 refers to the first step from compound (1) to compound (3). Four experiments were performed through which the amount of fuming  $\text{H}_2\text{SO}_4$  was increased (5.37 g to 21.5 g for 50 g of hexabutyldisiloxane). The products were analyzed by quantitative  $^{13}\text{C}$  and  $^{29}\text{Si}$  FT NMR. Subsequent analytical data were obtained by FT IR.

5

Figure 1 shows the decrease of (1) and the formation of (3) (=P1) and a minor amount of a second product (=P2). It is believed that this latter product could be a pyrosulfate ( $\text{Bu}_3\text{Si-O-SO}_2\text{-O-SO}_2\text{-O-SiBu}_3$ ).

10 The trialkylsilylated carboxylate monomers obtained by the process of the invention are useful in coating or paint composition. More preferably they are used in antifouling coating or paint compositions.

They can be polymerised with various other monomers such as vinyl monomers including  
15 acrylic esters, methacrylic esters, styrene, vinyl esters (e.g., vinyl acetate, vinyl propionate, vinyl butyrate, vinyl benzoate), vinyltoluene, alpha-methylstyrene, crotonic esters, and itaconic esters.

The polymers and copolymers of said monomers when used in a antifouling coating  
20 composition give a film which undergoes neither cracking nor peeling and shows moderate hydrolysability to dissolve into seawater constantly at an adequate rate and which therefore exhibits excellent antifouling property for long term.

The antifouling coating compositions prepared using the monomers obtained by the  
25 process of the invention are tin-free coatings and provide an alternative to the present self-polishing coating (spc) technology based on hydrolysable tributyltin polymers (use of which is due to be banned in antifouling paints by 2003). The trialkylsilylated carboxylate monomers provided by the process of the invention compared to organotin compounds are less toxic, less polar, more hydrophobic and more stable.

30

#### Examples

Hereunder four examples are given, the first two are comparative examples and the others are examples according to the invention. However it should be construed that the invention is in no way limited to those examples.

Example 1: First comparative example

Comparative example vis-à-vis the invention, according to the teaching of Chem. Lett. 1980, 1475-1478. The same procedure as described in that reference was applied using methacrylic acid, hexabutyldisiloxane and concentrated sulfuric acid as catalyst. In a flask  
5 equipped with a Dean-Stark extractor, are placed methacrylic acid 4.47 g, hexabutyldisiloxane 50 g, concentrated sulfuric acid as catalyst 0.5 g and toluene. After 7h of reflux in toluene using a Dean-Stark extractor, no trace of tributylsilylmethacrylate could however be detected.

10 Example 2: Second comparative example

The same procedure as described in Example 1 was performed using fuming sulfuric acid as catalyst. In a flask equipped with a Dean-Stark extractor, are placed methacrylic acid 4.47 g, hexabutyldisiloxane 50 g, fuming sulfuric acid as catalyst 0.9 g and toluene. The flask was heated to reflux. After 7h of reflux, no trace of tributylsilylmethacrylate could be  
15 detected.

Example 3: (Example according to the invention)

50 g of hexabutyldisiloxane (1) are added dropwise to 21.5 g of stirred fuming sulfuric acid (2) under a nitrogen atmosphere at 0°C, the reaction mixture is maintained at that  
20 temperature until the end of the addition. At that time the mixture is allowed to reach room temperature and stirred for an additional 18 h. After decantation, the upper layer is separated to furnish hexabutyldisilylsulfate (3).

1.9 g (2.1 equivalents) of sodium methacrylate (4) are added at 0°C at room temperature, to 4 g of stirred hexabutyldisilylsulfate (3) under an atmosphere of nitrogen. After 18 h at  
25 room temperature, dichloromethane is added and the sodium sulfate precipitate (6) is filtered out of the solution, the solvent is then evaporated to give tributylsilylmethacrylate (5) in a 73.3 % yield. The starting materials were found in the following amounts hexabutyldisiloxane 3.2%, hexabutyldisilylsulfate 4.9 %, and methacrylic acid 18.6%.

30

Example 4: (Example according to the invention)

10 g of hexamethyldisiloxane are added dropwise to 10.8 g of stirred fuming sulfuric acid (2) under a nitrogen atmosphere at 0°C, the reaction mixture is maintained at that temperature until the end of the addition. At that time the mixture is allowed to reach room

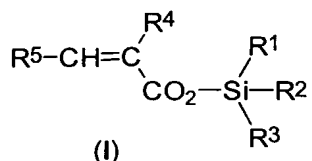
temperature and stirred for an additional 4 h. After that time, water is eliminated by addition of toluene and evaporation under vacuum to furnish hexamethyldisilylsulfate.

5 1.9 g (2.2 equivalents) of sodium methacrylate (4) are added, at room temperature, to 2 g of stirred hexamethyldisilylsulfate under an atmosphere of nitrogen. After 18 h at that temperature, dichloromethane is added and the sodium sulfate precipitate (6) is filtered out of the solution, the solvent is then evaporated to give trimethylsilylmethacrylate.

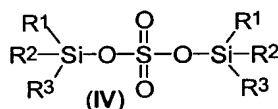
10 While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

## Claims

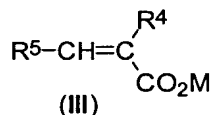
1. Process for the preparation of trialkylsilylated carboxylate monomers of general formula (I)



- wherein  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$  represents each independently an alkyl or an aryl group,  $\text{R}^4$  represents a hydrogen atom or a methyl group and  $\text{R}^5$  represents a hydrogen, alkyl,  $-\text{COR}^6$  or  $-\text{COOR}^6$ ; wherein  $\text{R}^6$  represents an alkyl group, which process comprises the step of reacting a hexaalkyldisilylsulfate of the formula (IV)

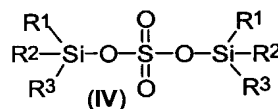


with an unsaturated carboxylic compound of formula (III)

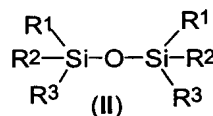


- wherein M is a metallic cation and  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$ ,  $\text{R}^4$ ,  $\text{R}^5$  have the same meaning as that defined above respectively.

2. A process for the preparation of a hexaalkyldisilylsulfate of the formula (IV)

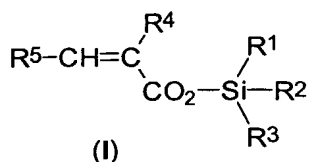


by treating a hexaalkyldisiloxane of formula (II)

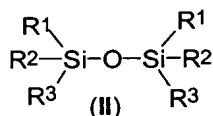


- with fuming sulfuric acid, wherein  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$  represents each independently an alkyl or an aryl group.

3. A process for the preparation of trialkylsilylated carboxylate monomers of general formula (I)



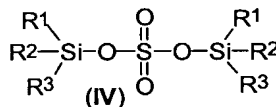
comprising a first step by treating a hexaalkyldisiloxane of formula (II)



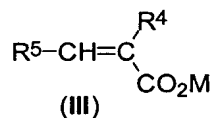
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with fuming sulfuric acid, according to claim 2, and

a second step by reacting a hexaalkyldisilylsulfate of the formula (IV)



with an unsaturated carboxylic compound of formula (III),



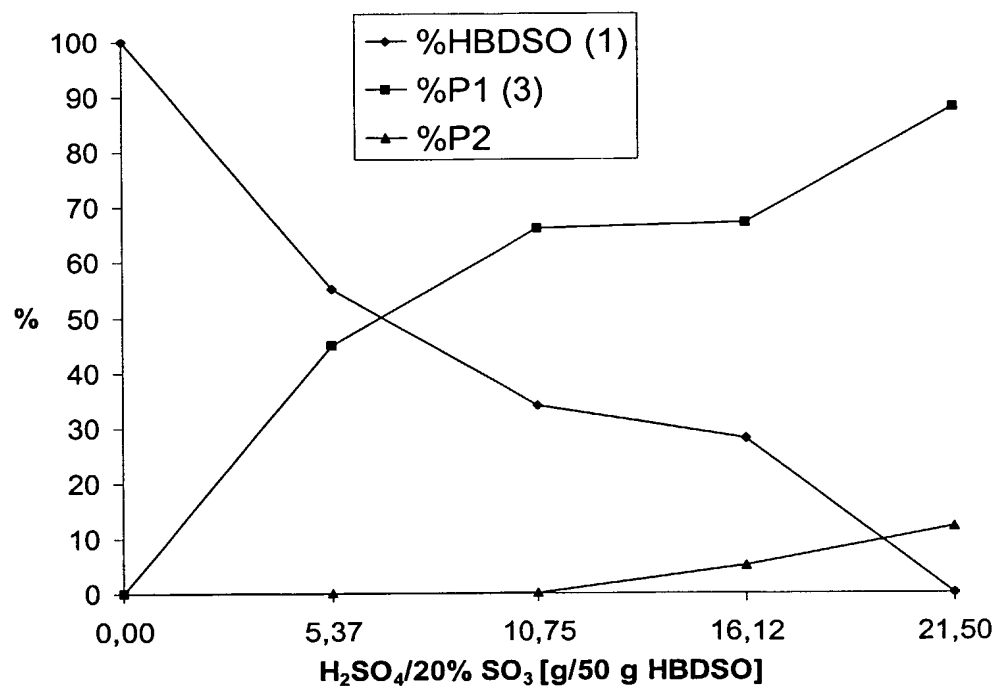
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according to claim 1, wherein M, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup> have the same meaning as that defined above respectively.

4. A process according to claims 1 to 3, wherein R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>6</sup> each independently is a linear, branched or cyclic alkyl group, saturated or unsaturated, containing from 1 to 12 carbon atoms, preferably from 1 to 6 carbon atoms, more preferably from 1 to 4 carbon atoms.
5. A process according to claim 4, wherein R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> each independently are chosen from the group comprising methyl, ethyl, propyl, isopropyl, butyl, t-butyl and phenyl.
6. A process according to claims 5, wherein R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> are butyl or isopropyl.
7. A process according to claims 1 or 3 to 6, wherein the unsaturated carboxylic compound of formula (III) chosen from the group comprising the metals salts and preferably is the sodium or the potassium salt.
8. A process according to claims 1 or 3 to 7, wherein the unsaturated carboxylic compound of formula (III), is chosen from the group comprising the salts of acrylic acid, methacrylic acid, maleic acid and fumaric acid.

9. A process according to claim 7 and 8, wherein the unsaturated carboxylic compound of formula (III), is preferably a methacrylic compound, more preferably sodium methacrylate.
10. A process according to claims 1 to 11, wherein the reaction steps are performed under inert atmosphere and preferably under nitrogen atmosphere.
11. A process according to claims 1 or 3 to 10, wherein the reaction product comprising the of trialkylsilylated carboxylate monomers of general formula (I) is further treated with an organic solvent and then filtered.
12. A process according to claim 11, wherein the organic solvent is a halogenated solvent, more preferably a chlorinated solvent and yet more preferably dichloromethane.
13. A process according to claims 11 or 12, wherein the formed trialkylsilylated carboxylate monomers of general formula (I) are obtained after evaporating the organic solvent.
14. A process according to claim 2, wherein the relative amount of fuming  $\text{H}_2\text{SO}_4$  is present in more than 0.5 eq., more preferably at about 1 equivalent.
15. Hexaalkyldisilylsulfate obtained by performing the process of claim 2.
16. Trialkylsilylated carboxylate monomers obtained by the process of any of claims 1 or 3 to 13.
17. Triisopropylsilyl methacrylate obtained by the process of any of claims 1 or 3 to 13.
18. Tributylsilyl methacrylate obtained by the process of any of claims 1 or 3 to 13.
19. Use of a compound obtained by the process of any of claims 1 to 13 in the preparation of a hydrolysable polymer.
20. Use according to claim 19 in antifouling coating compositions.

Fig. 1



# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP 02/05553

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC 7 C07F7/08 C07F7/18 C09D5/16 C08F4/42		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) IPC 7 C07F		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)  CHEM ABS Data		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CHEMICAL ABSTRACTS, vol. 97, no. 17, 25 October 1982 (1982-10-25) Columbus, Ohio, US; abstract no. 145006, YUKI GOSEI KOGYO CO., LTD., JAPAN: "Carboxylic acid trialkylsilyl esters" XP002180217 abstract & JP 57 040493 A (YUKI GOSEI KOGYO CO., LTD., JAPAN) 6 March 1982 (1982-03-06)	1, 3-13
X	MATSUMOTO, H. ET AL.: "a facile silylation of carboxylic acids with hexamethyldisiloxane" CHEMISTRY LETTERS, 1980, pages 1475-1478, XP002181505 cited in the application the whole document	1-15
<div style="display: flex; justify-content: space-between;"> <span><input checked="" type="checkbox"/> Further documents are listed in the continuation of box C.</span> <span><input checked="" type="checkbox"/> Patent family members are listed in annex.</span> </div>		
° Special categories of cited documents :		
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>*A* document defining the general state of the art which is not considered to be of particular relevance</p> <p>*E* earlier document but published on or after the international filing date</p> <p>*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>*O* document referring to an oral disclosure, use, exhibition or other means</p> <p>*P* document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>*&amp;* document member of the same patent family</p> </div> </div>		
Date of the actual completion of the international search  <div style="text-align: center; font-weight: bold;">3 September 2002</div>		Date of mailing of the international search report  <div style="text-align: center; font-weight: bold;">09/09/2002</div>
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl. Fax: (+31-70) 340-3016		Authorized officer  <div style="text-align: center; font-weight: bold;">Rinkel, L</div>



# INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 02/05553

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 775 733 A (CHUGOKU MARINE PAINTS, LTD) 28 May 1997 (1997-05-28) cited in the application the whole document -----	16-20

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/EP 02/05553

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:  
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☒ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

### Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

**FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210**

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1,3-13

Process for the preparation of trialkylsilylated carboxylate monomers

2. Claims: 2,14

Process for the preparation of hexaalkyldisilylsulfate

3. Claim : 15

Hexaalkyldisilylsulfate

4. Claims: 16-18

Trialkylsilylated carboxylate monomers

5. Claims: 19,20

Use of a trialkylsilylated carboxylate monomer in the preparation of a hydrolysable polymer

**WARNING:** Please note that were any or all of the further subjects elected for further processing, that further non-unity objections may be raised against these subjects based on subsequently retrieved prior art

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 02/05553

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
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			JP 63017835 B	15-04-1988
EP 775733	A	28-05-1997	EP 0775733 A1	28-05-1997
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			US 6172132 B1	09-01-2001
			JP 9048946 A	18-02-1997
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			JP 9048949 A	18-02-1997
			JP 9194790 A	29-07-1997